



U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.51) <b>UNASSIGNED 09/980216</b>		INTERNATIONAL APPLICATION NO. <b>PCT/FR00/01508</b>		ATTORNEY'S DOCKET NUMBER <b>022701-967</b>	
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21. <input checked="" type="checkbox"/> The following fees are submitted:	<b>CALCULATIONS</b>	PTO USE ONLY																
<b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1,040.00 (960) International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00 (970) International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$740.00 (958) International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$710.00 (956) International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00 (962)																		
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		\$ 890.00																
Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)).		\$																
20 <input type="checkbox"/> 30 <input type="checkbox"/>																		
<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <th style="width:20%;">Claims</th> <th style="width:20%;">Number Filed</th> <th style="width:20%;">Number Extra</th> <th style="width:40%;">Rate</th> </tr> <tr> <td>Total Claims</td> <td style="text-align: center;">22 - 20 =</td> <td style="text-align: center;">2</td> <td style="text-align: center;">X \$18.00 (966)</td> </tr> <tr> <td>Independent Claims</td> <td style="text-align: center;">6 - 3 =</td> <td style="text-align: center;">3</td> <td style="text-align: center;">X \$84.00 (964)</td> </tr> <tr> <td colspan="3" style="padding: 5px;">Multiple dependent claim(s) (if applicable)</td> <td style="text-align: center;">+ \$280.00 (968)</td> </tr> </table>	Claims	Number Filed	Number Extra	Rate	Total Claims	22 - 20 =	2	X \$18.00 (966)	Independent Claims	6 - 3 =	3	X \$84.00 (964)	Multiple dependent claim(s) (if applicable)			+ \$280.00 (968)	\$ 36.00	
Claims	Number Filed	Number Extra	Rate															
Total Claims	22 - 20 =	2	X \$18.00 (966)															
Independent Claims	6 - 3 =	3	X \$84.00 (964)															
Multiple dependent claim(s) (if applicable)			+ \$280.00 (968)															
<b>TOTAL OF ABOVE CALCULATIONS =</b>		\$ 288.00																
Reduction for 1/2 for filing by small entity, if applicable (see below).		+ \$ -																
<b>SUBTOTAL =</b>		\$ 1178.00																
Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)).		\$																
20 <input type="checkbox"/> 30 <input type="checkbox"/>																		
<b>TOTAL NATIONAL FEE =</b>		\$ 1178.00																
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property		+ \$																
<b>TOTAL FEES ENCLOSED =</b>		\$ 1178.00																
		Amount to be refunded: \$																
		charged: \$																

a. ☐ Small entity status is hereby claimed.

b. ☒ A check in the amount of \$ 1,178.00 to cover the above fees is enclosed.

c. ☐ Please charge my Deposit Account No. 02-4800 in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

d. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4800. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

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Patent

Attorney's Docket No. 022701-967

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of )  
Alain DEMOURGUES *et al.* ) Group Art Unit: (Unassigned)  
Application No.: UNASSIGNED ) Examiner: (Unassigned)  
(Corresponds to PCT/FR00/01508) )  
International Filing Date: 31 MAY 2000 )  
For: RARE EARTH FLUOROSULPHIDES )  
OR OXYFLUOROSULPHIDES, )  
METHODS FOR PREPARING SAME )  
AND USE THEREOF AS DYEING )  
PIGMENT )

PRELIMINARY AMENDMENT

**BOX PCT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-captioned application as follows:

**IN THE CLAIMS:**

Kindly amend claims 1-12 and 14-22 as follows:

1. (Amended) Rare earth fluorosulphide of the formula  $\text{LnSF}$ , in which Ln designates a rare earth having an average particle size of not more than  $5 \mu\text{m}$ .
2. (Amended) Process for the preparation of a fluorosulphide according to claim 1, wherein a rare earth oxyfluoride of the formula  $\text{LnOF}$  is reacted with a mixture of hydrogen sulphide and carbon disulphide.

3. (Amended) Process according to claim 2, wherein the reaction is carried out at a temperature between 500°C and 1,200°C.
4. (Amended) Mixed fluorosulphide of rare earths of the formula (Ln,Ln')SF in which Ln and Ln' designated two rare earths, and in the form of a solid solution.
5. (Amended) Fluorosulphide according to claim 4, corresponding to the formula (Ln<sub>0.66</sub>, Ln'<sub>0.33</sub>)SF.
6. (Amended) Fluorosulphide according to claim 4, wherein Ln and Ln' are selected from the group consisting of cerium, samarium, praseodymium and gadolinium.
7. (Amended) Process for the preparation of a fluorosulphide according to claim 5, comprising reacting a sulphide of one rare earth Ln<sub>2</sub>S<sub>3</sub> with a fluoride of the other rare earth Ln'F<sub>3</sub>.
8. (Amended) Process according to claim 7, wherein the reaction is carried out at a temperature between 800°C and 1,200°C.
9. (Amended) Process for the preparation of a fluorosulphide according to claim 4, comprising reacting a mixed oxyfluoride of rare earths of the formula (LnLn')OF with a mixture of hydrogen sulphide and carbon disulphide.

10. (Amended) Rare earth fluorosulphide, comprising at least one alkali element, and having a structure of the type  $\text{LnSF}$ , tetragonal, space group  $P4/nmm$ ,  $\text{Ln}$  designating a rare earth chosen from the group consisting of yttrium and the rare earths  $\text{Ln}$  between lanthanum and erbium inclusive.

11. (Amended) Rare earth fluorosulphide comprising at least on alkali element, and having a hexagonal structure, space group  $P6_322$ , the rare earth belonging to the group of rare earths between holmium and lutecium inclusive and including yttrium.

12. (Amended) Process for the preparation of a fluorosulphide according to claim 10, wherein a rare earth sulphide of the formula  $\text{Ln}_2\text{S}_3$  comprises at least one alkaliis and is reacted with a fluoride of the same rare earth.

14. (Amended) Fluorosulphide according to claim 13, wherein the alkaline earth is calcium or strontium.

15. (Amended) Fluorosulphide according to claim 13, wherein the rare earth is cerium or samarium.

16. (Amended) Process for the preparation of a rare earth fluorosulphide according to claim 15, wherein a rare earth sulphide is reacted with a chloride of the same rare earth and a fluoride of the alkaline earth element.

17. (Amended) Process for the preparation of a rare earth fluorosulphide according to claim 15, wherein the rare earth in the form of the metal is reacted with sulphur, a fluoride of the same rare earth and a fluoride of the alkaline earth element.
18. (Amended) Rare earth oxyfluorosulphide, corresponding to the formula  $\text{Ln}_3\text{S}_2\text{F}_3\text{O}$ , in which Ln represents at least one trivalent rare earth.
19. (Amended) Process for the preparation of an oxyfluorosulphide according to claim 18, comprising reacting an oxide of the rare earth, a sulphide of the same rare earth  $\text{Ln}_2\text{S}_3$  and a fluoride of this rare earth.
20. (Amended) A colouring pigment comprising fluorosulphide or an oxyfluorosulphide according to claim 1.
21. (Amended) A colouring pigment in plastics materials, paints, finishes, rubbers, ceramics, glazes, papers, inks, cosmetics products, dyestuffs, in the finishing of leathers and in laminated coverings comprising a fluorosulphide or an oxyfluorosulphide according to claim 1.
22. (Amended) Coloured material compositions comprising a fluorosulphide or an oxyfluorosulphide according to claim 1.

**REMARKS**

Entry of the foregoing amendment(s) is respectfully requested.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

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By: 

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**Date: November 30, 2001**

**Attachment to Preliminary Amendment dated November 30, 2001**

**Marked-up Claims 1-12 and 14-22**

1. Rare earth fluorosulphide of the formula  $\text{LnSF}$ , in which Ln designates a rare earth [characterized in that it has] having an average particle size of not more than 5  $\mu\text{m}$ .
2. Process for the preparation of a fluorosulphide according to claim 1, [characterized in that] wherein a rare earth oxyfluoride of the formula  $\text{LnOF}$  is reacted with a mixture of hydrogen sulphide and carbon disulphide.
3. Process according to claim 2, [characterized in that] wherein the reaction is carried out at a temperature between  $500^{\circ}\text{C}$  and  $1,200^{\circ}\text{C}$ [, preferably between  $900^{\circ}\text{C}$  and  $1,000^{\circ}\text{C}$ ].
4. Mixed fluorosulphide of rare earths of the formula  $(\text{Ln}, \text{Ln}')\text{SF}$  in which Ln and Ln' designated two rare earths, [characterized in that it is] and in the form of a solid solution.
5. Fluorosulphide according to claim 4, [characterized in that it corresponds] corresponding to the formula  $(\text{Ln}_{0.66}, \text{Ln}'_{0.33})\text{SF}$ .
6. Fluorosulphide according to [one of claims 4 or 5] claim 4, [characterized in that] wherein Ln and Ln' are [chosen] selected from the group consisting of cerium, samarium, praseodymium and gadolinium.

**Attachment to Preliminary Amendment dated November 30, 2001**

### Marked-up Claims 1-12 and 14-22

7. Process for the preparation of a fluorosulphide according to claim 5, [characterized in that] ~~comprising reacting~~ a sulphide of one rare earth  $\text{Ln}_2\text{S}_3$  [is reacted] with a fluoride of the other rare earth  $\text{Ln}'\text{F}_3$ .
8. Process according to claim 7, [characterized in that] ~~wherein~~ the reaction is carried out at a temperature between  $800^\circ\text{C}$  and  $1,200^\circ\text{C}$ [, preferably between  $900^\circ\text{C}$  and  $1,000^\circ\text{C}$ ].
9. Process for the preparation of a fluorosulphide according to [one of claims 4 to 6] claim 4, [characterized in that] ~~comprising reacting~~ a mixed oxyfluoride of rare earths of the formula  $(\text{LnLn}')\text{OF}$  [is reacted] with a mixture of hydrogen sulphide and carbon disulphide.
10. Rare earth fluorosulphide, [characterized in that it comprises] ~~comprising~~ at least one alkali element, and [in that it has] ~~having~~ a structure of the type  $\text{LnSF}$ , tetragonal, space group  $\text{P4/nmm}$ , Ln designating a rare earth chosen from the group consisting of yttrium and the rare earths Ln between lanthanum and erbium inclusive.
11. Rare earth fluorosulphide[, characterized in that it comprises] ~~comprising~~ at least one alkali element, and [in that it has] ~~having~~ a hexagonal structure, space group  $\text{P6}_322$ , the rare earth belonging to the group of rare earths between holmium and lutecium inclusive and [also] including yttrium.

**Attachment to Preliminary Amendment dated November 30, 2001**

**Marked-up Claims 1-12 and 14-22**

12. Process for the preparation of a fluorosulphide according to claim 10 [or 11], [characterized in that] wherein a rare earth sulphide of the formula  $\text{Ln}_2\text{S}_3$  [comprising] comprises at least one alkaliis and is reacted with a fluoride of the same rare earth.

14. Fluorosulphide according to claim 13, [characterized in that] wherein the alkaline earth is calcium or strontium.

15. Fluorosulphide according to claim 13, [or 14, characterized in that] wherein the rare earth is cerium or samarium.

16. Process for the preparation of a rare earth fluorosulphide according to [one of claims 13 to 15] claim 15, [characterized in that] wherein a rare earth sulphide is reacted with a chloride of the same rare earth and a fluoride of the alkaline earth element.

17. Process for the preparation of a rare earth fluorosulphide according to [one of claims 13 to 15] claim 15, [characterized in that] wherein the rare earth in the form of the metal is reacted with sulphur, a fluoride of the same rare earth and a fluoride of the alkaline earth element.

18. Rare earth oxyfluorosulphide, [characterized in that it corresponds] corresponding to the formula  $\text{Ln}_3\text{S}_2\text{F}_3\text{O}$ , in which Ln represents at least one trivalent rare earth.

**Attachment to Preliminary Amendment dated November 30, 2001**

### Marked-up Claims 1-12 and 14-22

19. Process for the preparation of an oxyfluorosulphide according to claim 18,  
[characterized in that] comprising reacting an oxide of the rare earth, a sulphide of the same  
rare earth  $\text{Ln}_2\text{S}_3$  and a fluoride of this rare earth [are reacted].

20. [Use of a fluorosulphide or an oxyfluorosulphide according to one of claims 1, 4 to 6, 10 to 11, 13 to 15 and 18 as a] A colouring pigment comprising fluorosulphide or an oxyfluorosulphide according to claim 1.

21. [Use of a fluorosulphide or an oxyfluorosulphide according to one of claims 1, 4 to 6, 10 to 11, 13 to 15 and 18 as a] A colouring pigment in plastics materials, paints, finishes, rubbers, ceramics, glazes, papers, inks, cosmetics products, dyestuffs, in the finishing of leathers and in laminated coverings comprising a fluorosulphide or an oxyfluorosulphide according to claim 1.

22. Coloured material compositions[, in particular of the following type:  
plastics, paints, finishes, rubbers, ceramics, glazes, papers, inks, cosmetics products,  
dyestuffs and laminated coverings, characterized in that they comprise] comprising a  
fluorosulphide or an oxyfluorosulphide according to [one of claims 1, 4 to 6, 10 to 11, 13  
to 15 and 18] claim 1.

**NEW RARE EARTH FLUOROSULPHIDES OR OXYFLUOROSULPHIDES,**  
**PROCESSES FOR THEIR PREPARATION AND THEIR USE AS A COLOURING**  
**PIGMENT**

5 **RHODIA CHIMIE**

The present invention relates to new rare earth fluorosulphides and new rare earth oxyfluorosulphides, processes for their preparation and their use as a colouring pigment in particular.

10

Mineral colouring pigments are already widely used in several industries, in particular those of paints, plastics materials and ceramics. In such applications, properties such as, inter alia, the heat and/or chemical stability, the dispersibility (ability of the product to disperse correctly in a given medium), the intrinsic colour, the colouring power and the opacifying power, constitute so much the criteria which it is particularly important to take into consideration in the choice of a suitable pigment.

15

Unfortunately, the problem is that the majority of mineral pigments which are suitable for applications such as those above and which have been used effectively to date on an industrial scale generally make use of metals (cadmium, lead, chromium and cobalt in particular) the use of which is becoming more and more severely regulated, and even banned, by the legislations of several countries, taking into account in effect their very high reputed toxicity. There may thus be mentioned more particularly, by way of non-limitative examples, the case of red pigments based on cadmium selenide and/or cadmium sulphoselenide, for which substitutes based on rare earth sulphides have already been proposed by the Applicant. Compositions based on sesquisulphides of a rare earth and alkali elements have thus been described in EP-A-545746. These compositions have proved to be particularly interesting substitutes.

25

However, the need has arisen for an even wider range of products of pigmentary quality.

30

The object of the invention is therefore to provide new products of the rare earth fluorosulphides type.

For this purpose, according to a first embodiment the rare earth fluorosulphide of the invention corresponds to the formula  $\text{LnSF}_6$ , in which Ln designates a rare earth, and it is characterized in that it has an average particle size of not more than 5  $\mu\text{m}$ .

5 According to a second embodiment the fluorosulphide of the invention is a mixed fluorosulphide of rare earths of the formula  $(\text{Ln}, \text{Ln}')\text{SF}_6$ , in which Ln and Ln' designate two rare earths, and it is characterized in that it is in the form of a solid solution.

10 According to a third embodiment the invention also relates to a rare earth fluorosulphide which, according to a first variant, is characterized in that it comprises at least one alkali element and in that it has a structure of the  $\text{LnSF}_6$  type, tetragonal, space group  $\text{P4/nmm}$ , Ln designating a rare earth chosen from the group consisting of yttrium and the rare earths between lanthanum and erbium inclusive. According to a second variant of this third embodiment, the rare earth fluorosulphide is characterized in that it comprises at least one  
15 alkali element and in that it has a hexagonal structure, space group  $\text{P6}_322$ , the rare earth belonging to the group of rare earths between holmium and lutecium inclusive and also including yttrium.

20 Furthermore, according to a fourth embodiment the rare earth fluorosulphide of the invention corresponds to the formula  $\text{Ln}_2\text{AF}_4\text{S}_2$ , in which Ln designates at least one rare earth and A designates at least one alkaline earth.

25 Finally, the invention also relates to a rare earth oxyfluorosulphide, characterized in that it corresponds to the formula  $\text{Ln}_3\text{S}_2\text{F}_3\text{O}$ , in which Ln represents at least one trivalent rare earth.

Other characteristics, details and advantages of the invention will appear still more completely on reading the description which follows and the various concrete but non-limitative examples intended to illustrate it.

30

It is first stated here and for all the description, unless indicated otherwise, that rare earth is understood as meaning the elements of the group consisting of yttrium and the elements of the periodic table of atomic number between 57 and 71 inclusive.

It is also stated that the fluorosulphides of the invention are products fluorinated in the mass, that is to say the fluorine is present in the entirety or all the mass of the products and not solely or essentially on the surface thereof.

5 The first embodiment of the invention will now be described.

As indicated above, the product according to this first embodiment is a fluorosulphide of the formula  $\text{LnSF}$ . Ln, the rare earth, can be more particularly lanthanum, cerium, praseodymium, neodymium, samarium or gadolinium. The main characteristic of this  
10 product is its granulometry. The average particle size ( $d_{50}$ ) is not more than  $5\text{ }\mu\text{m}$ , more particularly not more than  $2\text{ }\mu\text{m}$ . The average size is the value obtained using the laser diffraction technique with an apparatus of the type Coulter LS 230 on a product which has been subjected to deagglomeration under gentle conditions.

15 This product can be either of a tetragonal  $\text{P4/nmm}$  structure, in the case of a rare earth of the group from lanthanum to erbium, including yttrium, or a hexagonal  $\text{P6}_322$  structure, in the case of a rare earth of the group from holmium to lutecium, including yttrium.

The process for the preparation of the product according to the first embodiment will  
20 now be described.

The process is characterized in that a rare earth oxyfluoride of the formula  $\text{LnOF}$  is reacted with a mixture of hydrogen sulphide and carbon disulphide.

25 The rare earth oxyfluoride can be obtained by reaction of the rare earth oxide with the fluoride of the same rare earth, generally at about  $800^\circ\text{C}$ , under an inert atmosphere. The temperature is increased, for example, at a rate of  $1^\circ\text{C}/\text{min}$  and may be kept at the level for 48 hours. If necessary, the product is ground to a granulometry at most equal to that of the sulphurized product to be obtained.

30

In general, the mixture of hydrogen sulphide and carbon disulphide is used with an inert gas, such as argon or nitrogen. The respective proportions of hydrogen sulphide and carbon disulphide can be as desired. In general, the partial pressure of these gases is between

0.1.10<sup>5</sup> Pa and 1.10<sup>5</sup> Pa.

The reaction is usually carried out at a temperature between 500°C and 1,200°C, preferably between 700°C and 850°C. The duration of the reaction corresponds to the time required to obtain the desired fluorosulphide, and this duration is shorter the higher the temperature.

The product obtained at the end of the reaction usually has an average size of not more than 5 µm. However, if this is not the case or if a finer granulometry is desired, the product can be deagglomerated. Deagglomeration under gentle conditions is sufficient to obtain an average size which can be less than the starting size.

The product according to the second embodiment of the invention will now be described. This product is a mixed fluorosulphide of rare earths of the formula (Ln,Ln')SF, in which Ln and Ln' designate two different rare earths. These rare earths can be more particularly a combination of cerium, gadolinium, samarium and praseodymium. The two rare earths can be in any desired respective proportions. According to a particular embodiment the fluorosulphide corresponds to the formula (Ln<sub>0.66</sub>,Ln'<sub>0.33</sub>)SF.

The structure of this product varies as a function of Ln and Ln' in particular. It is either tetragonal P4/nmm or hexagonal P6<sub>3</sub>22.

The product is characterized in that it is in the form of a solid solution, that is to say a solid solution of the two rare earths in an LnSF crystal cell. This characteristic can be demonstrated by X-ray analysis. It is also pointed out that the volume of the unit cell V of fluorosulphide practically corresponds to the average volume of the unit cell of each of the fluorosulphides LnSF and Ln'SF in the case where the two fluorosulphides are of the same tetragonal or hexagonal crystal structure.

The fluorosulphide of this second embodiment can be prepared by two different routes.

According to a first method, a sulphide of one rare earth Ln<sub>2</sub>S<sub>3</sub> is reacted with a

fluoride of the other rare earth  $\text{LnF}_3$ . The reaction is usually carried out at a temperature between  $800^\circ\text{C}$  and  $1,200^\circ\text{C}$ , preferably between  $900^\circ\text{C}$  and  $1,000^\circ\text{C}$ . It is preferably carried out in vacuo. The duration of the reaction corresponds to the time required to obtain the desired fluorosulphide. This method leads to the fluorosulphide of the formula  
5  $(\text{Ln}_{0.66}, \text{Ln}'_{0.33})\text{SF}$ .

A second possible method for the preparation of a fluorosulphide according to the second embodiment comprises reacting a mixed oxyfluoride of rare earths of the formula  $(\text{Ln}, \text{Ln}')\text{OF}$  with a mixture of hydrogen sulphide and carbon disulphide. The conditions  
10 under which this reaction is carried out are the same as those described above for the preparation of the fluorosulphide according to the first embodiment.

The invention also relates to a fluorosulphide according to a third embodiment. In this case, and according to a first variant, it is a fluorosulphide of a rare earth chosen from the group consisting of yttrium and the rare earths between lanthanum and erbium inclusive. The  
15 product is characterized in that it comprises at least one alkali element and in that it has a structure of the type  $\text{LnSF}$ , tetragonal, space group  $\text{P4/nmm}$ . According to a second variant, it is a fluorosulphide of a rare earth chosen from the group consisting of the rare earths between holmium and lutecium inclusive and also including yttrium. In this case, the  
20 structure of the product is of the hexagonal type, space group  $\text{P6}_322$ .

The alkali element can be chosen in particular from lithium, sodium or potassium. The fluorosulphide of the invention can of course also comprise several alkali elements, and all that described with reference to an alkali thus also applies in the case where several alkali  
25 metals are present.

According to a preferred embodiment of the invention this alkali element is included at least in part in the fluorosulphide crystal lattice. According to one variant of this  
30 embodiment the alkali element is included substantially or totally in the crystal lattice.

The process for the preparation of the fluorosulphide according to this third embodiment comprises reacting a rare earth sulphide of the formula  $\text{Ln}_2\text{S}_3$  comprising at least one alkali with a fluoride of the same rare earth. The starting rare earth sulphide can be a sulphide of the type of those described in the patent applications EP-A-545746, EP-A-680930

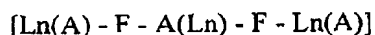
and WO 99/07639, the disclosure of which is incorporated here. More particularly, it is possible to use the sulphides described in EP-A-680930, which are obtained by a process using a rare earth carbonate or hydroxycarbonate with hydrogen sulphide or carbon disulphide or a mixture of the two. WO 99/07639 describes a samarium sesquisulphide of high purity which may also be an interesting starting substance.

It will be noted here that in the case of this third embodiment, as for the second embodiment which has been described above, whether a hexagonal or tetragonal structure is obtained depends on the type of cooling to which the product is subjected after the reaction. Thus, if the cooling is slow, the hexagonal structure (P6<sub>3</sub>22) is obtained, while if the cooling is rapid (quenching), the tetragonal structure (P4/nmm) is obtained.

The reaction of the rare earth sulphide with the fluoride is usually carried out at a temperature between 800°C and 1,200°C, preferably between 900°C and 1,000°C. It is preferably carried out in vacuo. The duration of the reaction corresponds to the time required to obtain the desired fluorosulphide.

The invention also relates to a fourth embodiment. In this case, the rare earth fluorosulphide corresponds to the formula Ln<sub>2</sub>AlF<sub>4</sub>S<sub>2</sub>, in which Ln designates at least one rare earth and A designates at least one alkaline earth. The alkaline earth can be more particularly calcium or strontium. The rare earth can be, in particular, cerium or samarium.

This fluorosulphide has a tetragonal 14/mmm leaf structure. These leaves [Ln<sub>2</sub>AlF<sub>4</sub>]<sup>4+</sup> are made up of different layers of rare earth and alkaline earth atoms separated from one another by layers of fluorine atoms according to the sequence:



the cation in parentheses indicating the cationic disorder within the various layers, and the leaves are separated from one another by double layers of sulphur atoms [S<sub>2</sub>]<sup>4-</sup>.

The preparation of the fluorosulphide according to this fourth embodiment can be carried out by two methods. In a first case, a rare earth sulphide is reacted with a fluoride of the same rare earth and a fluoride of the alkaline earth element. In a second case, the rare

earth in the form of the metal is reacted with sulphur, a fluoride of the same rare earth and a fluoride of the alkaline earth element. In both cases the reaction temperature is generally between 1,000°C and 1,300°C, more particularly between 1,150°C and 1,200°C. The reaction is preferably carried out in vacuo.

5

Finally, the invention also relates to a rare earth oxyfluorosulphide of the formula  $\text{Ln}_3\text{S}_2\text{F}_3\text{O}$ , in which Ln represents at least one trivalent rare earth. There may be mentioned more particularly cerium as the trivalent rare earth. These products have a lamellar structure derived from the lattice of the  $\text{Ln}_2\text{AF}_4\text{S}_2$  phase described above.

10

The oxyfluorides of the invention can be prepared by reaction of the rare earth oxide, the sulphide of the same rare earth  $\text{Ln}_2\text{S}_3$  and the rare earth fluoride. The reaction is usually carried out at a temperature between 800°C and 1,200°C. It is preferably carried out in vacuo. The duration of the reaction corresponds to the time required to obtain the desired product.

15

An oxyfluorosulphide of the more particular composition  $\text{Ln}_{2.33}\text{Ln}'_{0.66}\text{S}_2\text{F}_3\text{O}$ , where Ln and Ln' designate two different rare earths, can be obtained by reaction of a rare earth fluoride  $\text{LnF}_3$  (1), the sulphide  $\text{Ln}_2\text{S}_3$  (2/3) of the same rare earth and an oxide  $\text{Ln}'_2\text{O}_3$  (1/3) of the other rare earth in the stoichiometric proportions stated in parentheses.

20

The fluorosulphides and the oxyfluorosulphides of the invention can be used as a colouring pigment.

Thus, and still more precisely, they can be used in the coloration of plastics materials, which can be of the thermoplastic or thermosetting type.

25

Thermoplastic resins which can be coloured according to the invention and which may be mentioned, purely by way of illustration, are polyvinyl chloride, polyvinyl alcohol, polystyrene, styrene/butadiene, styrene/acrylonitrile and acrylonitrile/butadiene/styrene (ABS) copolymers, acrylic polymers, in particular poly(methyl methacrylate), polyolefins, such as polyethylene, polypropylene, polybutene and polymethylpentene, cellulosic derivatives, such as, for example, cellulose acetate, cellulose acetobutyrate and ethylcellulose, and polyamides, such as polyamide 6-6.

30

As regards the thermosetting resins for which the fluorosulphides or oxyfluorosulphides according to the invention are also suitable, there may be mentioned, for example, phenoplasts, aminoplasts, in particular urea/formol and melaminic/formol copolymers, epoxy resins and thermosetting polyesters.

5

The fluorosulphides or the oxyfluorosulphides of the invention can also be used in special polymers, such as fluorinated polymers, in particular polytetrafluoroethylene (PTFE), polycarbonates, silicone elastomers and polyimides.

10

In this specific application for coloration of plastics, the fluorosulphides or oxyfluorosulphides of the invention can be used directly in the form of powders. They can also, preferably, be used in a pre-dispersed form, for example in a premix with some of the resin, in the form of a concentrated paste or a liquid, which enables them to be introduced at any stage of the production of the resin.

15

The fluorosulphides or oxyfluorosulphides according to the invention can thus be incorporated into plastics materials such as those mentioned above in a proportion by weight ranging generally either from 0.01 to 5% (based on the final product) or 40 to 70%, in the case of a concentrate.

20

The fluorosulphides or the oxyfluorosulphides of the invention can also be used in the field of paints and varnishes, and more particularly in the following resins: alkyd resins, the most common of which is called glycerophthalic resin; modified long or short oil resins; acrylic resins derived from esters of acrylic acid (methyl or ethyl) and methacrylic acid, possibly copolymerized with ethyl, 2-ethylhexyl or butyl acrylate; vinyl resins, such as, for example, polyvinyl acetate, polyvinyl chloride, polyvinylbutyral, polyvinylformal and copolymers of vinyl chloride and vinyl acetate or vinylidene chloride; aminoplast or phenolic resins, most often modified; polyester resins; polyurethane resins; epoxy resins; and silicone resins.

30

In general, the fluorosulphides or oxyfluorosulphides are used in an amount of 5 to 30% by weight of paint and 0.1 to 5% by weight of varnish.

Finally, the fluorosulphides or the oxyfluorosulphides according to the invention may

also be suitable for applications in the rubber industry, in particular floor coverings, in the paper and printing inks industry, in the field of cosmetics, and numerous other uses, such as, for example, and non-limitatively, dyestuffs, finishing of leathers and laminated coverings for kitchens and other work areas, ceramics and glazes.

5

The invention also relates to coloured material compositions, in particular of the type of plastics, paints, varnishes, rubbers, ceramics, glazes, papers, inks, cosmetics products, dyestuffs and laminated coverings, characterized in that they comprise a fluorosulphide or an oxyfluorosulphide of the type described above.

10

Finally, the oxyfluorosulphides of the invention can also be used as insulating supports for microelectronic devices and as lubricating agents.

Examples will now be given.

15

The procedure followed for measurement of the granulometry of the products is described below. A Laser COULTER LS 230 apparatus in the following configuration is used:

Standard module

20

Stirring speed: 64

Optical model  $Cc_2S_3$ :

750 nm	2.724	0
450 nm	3.011	0.099
600 nm	2.879	0.013
900 nm	2.7	0

25

The procedure is as follows:

30

- Prepare a 1 g/l solution of sodium hexametaphosphate.
- Add 60 mg powder to 50 ml of the above solution.
- Obtain a suspension by ultrasonic treatment (12 mm probe immersed 3 cm) for 3 minutes (power = graduation 7 of the potentiometer).
- Pour all the deagglomerated suspension into the measuring cell.
- Homogenize for 1 minute.

- Start the analysis.

For the colorimetric properties, the diffuse reflection spectra were recorded on a 900 spectrophotometer from Perkin-Elmer equipped with a biconical attachment. The values L, a and b were calculated from the diffuse reflection spectra according to the known mathematical formulae. R400 and R700 designate the absorptions at 400 and 700 nm.

The nature of the illuminant is D65, and the observation conditions correspond to viewing under an aperture angle of 10°. In the measurements given, the reflective component is excluded.

#### Example 1

This example relates to the preparation of a fluorosulphide according to the first embodiment of the invention.

A gadolinium oxyfluoride GdOF which was obtained by firing from a mixture of gadolinium oxide ( $Gd_2O_3$ ) and a gadolinium fluoride  $GdF_3$  is used. This mixture is heated to 800°C (1°C/min) under argon without flushing and kept at this temperature for 48 hours. The product thus obtained is then subjected to moist grinding in a mill with 5 mm zirconium beads and at the end of this grinding it has a granulometry of 2 µm. This product is then heated to 800°C at a rate of increase in temperature of 5°C/min, while flushing with a gas mixture at 2 l/h. This mixture comprises 74.5% argon, 12.75% carbon disulphide and 12.75% hydrogen sulphide. The product is left at 800°C for 1 hour and then brought to room temperature under a nitrogen atmosphere.

The product obtained has an average size of 2 µm.

#### Examples 2 to 6

These examples relate to the preparation of mixed fluorosulphides according to the second embodiment of the invention.

A lanthanum sulphide  $\text{Ln}_2\text{S}_3$  and a fluoride  $\text{Ln}'\text{F}_3$  are mixed in stoichiometric amounts in a vitreous carbon crucible closed by a graphite cover. The crucible is introduced into a quartz tube which is then sealed under vacuum. The crucible is then brought to a temperature of between  $900^\circ\text{C}$  and  $1,000^\circ\text{C}$  for 24 hours.

5

The formulae, the cell parameters and the space groups of the products obtained are given below in table 1 and the volumes and weighted volumes of the unit cells which confirm the formation of a solid solution are given below in table 1 a.

10

Table 1

Example	Formula	Cell parameters ( $\text{\AA}$ )	Space group
2	$\text{Ce}_{0.66}\text{Pr}_{0.33}\text{SF}$	$a=3.9796(2)$ ; $c=6.9363(5)$	P4/nmm
3	$\text{Gd}_{0.66}\text{Sm}_{0.33}\text{SF}$	$a=3.4849(1)$ ; $c=6.864(2)$	P4/nmm
4	$\text{Ce}_{0.66}\text{Sm}_{0.33}\text{SF}$	$a=3.9473(3)$ ; $c=6.9169(6)$	P4/nmm
5	$\text{Ce}_{0.66}\text{Gd}_{0.33}\text{SF}$	$a=3.938(1)$ ; $c=6.914(1)$	P4/nmm
6	$\text{Sm}_{0.66}\text{Gd}_{0.33}\text{SF}$	$a=3.859(1)$ ; $c=6.870(1)$	P4/nmm

Table 1 a

Example	Formula	Volume ( $\text{\AA}^3$ )	Weighted volume calculated from $\text{LnSF}$ ( $\text{\AA}^3$ )
2	$\text{Ce}_{0.66}\text{Pr}_{0.33}\text{SF}$	109.85	109.88
3	$\text{Gd}_{0.66}\text{Sm}_{0.33}\text{SF}$	101.69	101.37
4	$\text{Ce}_{0.66}\text{Sm}_{0.33}\text{SF}$	107.77	108.10
5	$\text{Ce}_{0.66}\text{Gd}_{0.33}\text{SF}$	107.22	107.22
6	$\text{Sm}_{0.66}\text{Gd}_{0.33}\text{SF}$	102.31	102.23

15

The colorimetric properties of the products are given in table 1 b below.

Table 1 b

Example	Formula	L	a	b	Colour	R400 (%)	R700 (%)
2	$\text{Ce}_{0.66}\text{Pr}_{0.33}\text{SF}$	41.9	30.9	23.4	red	5.2	43.3
4	$\text{Ce}_{0.66}\text{Sm}_{0.33}\text{SF}$	38.8	44.0	28.3	red	2.9	55.9
5	$\text{Ce}_{0.66}\text{Gd}_{0.33}\text{SF}$	37.0	41.2	28.0	red	3.1	50.0
6	$\text{Sm}_{0.66}\text{Gd}_{0.33}\text{SF}$	78.0	-8.3	73.8	yellow	3.2	63.2

## Examples 7 to 13

5

These examples relate to the preparation of mixed fluorosulphides according to the fourth embodiment of the invention. These products were obtained by reaction of stoichiometric amounts of a rare earth sulphide with a fluoride of the same rare earth and a fluoride of the alkaline earth element in a quartz tube sealed under vacuum at 1,200°C for 24

10 hours.

The formulae, the cell parameters and the space groups of the products obtained are given in table 2 below.

15

Table 2

Example	Formula	Cell parameters (Å)	Space group
7	$\text{Ce}_2\text{SrF}_4\text{S}_2$	$a=4.0782(2)$ ; $c=19.637(1)$	14/mmm
8	$\text{Nd}_2\text{SrF}_4\text{S}_2$	$a=4.025(5)$ ; $c=19.440(5)$	14/mmm
9	$\text{Sm}_2\text{SrF}_4\text{S}_2$	$a=4.005(1)$ ; $c=19.393(1)$	14/mmm
10	$\text{Ce}_2\text{CaF}_4\text{S}_2$	$a=3.967(1)$ ; $c=19.399(4)$	14/mmm
11	$\text{Nd}_2\text{CaF}_4\text{S}_2$	$a=3.942(2)$ ; $c=19.321(5)$	14/mmm
12	$\text{Sm}_2\text{CaF}_4\text{S}_2$	$a=3.91594(5)$ ; $c=19.2530(5)$	14/mmm
13	$\text{Pr}_2\text{CaF}_4\text{S}_2$	$a=3.955(2)$ ; $c=19.360(5)$	14/mmm

The colorimetric properties of the products are given in table 2 a below.

Table 2 a

Example	Formula	L	a	b	R400 (%)	R700 (%)
7	$\text{Ce}_2\text{SrF}_4\text{S}_2$	49.9	25.9	35.5	4.0	32.4
10	$\text{Ce}_2\text{CaF}_4\text{S}_2$	25.5	8.9	19.5		
13	$\text{Pr}_2\text{CaF}_4\text{S}_2$	49.9	-5.8	23.0	4.3	22.3

## 5 Example 14

The purpose of this example is to illustrate the chemical resistance to various acids of some products of the invention and of the prior art.

10 Solutions of hydrochloric acid (1.2 M), nitric acid (1.1 M) and sulphuric acid (1.8 M) are used. Two rare earth sulphides of the type  $\text{Th}_3\text{P}_4$  of the formula  $\text{Ce}_{2.5}\text{Li}_{0.5}\text{S}_4$  and  $\text{Ce}_2\text{SrS}_4$  are used by way of comparison. The product according to the invention is that of example 4. The results are given in table 3 below.

15 Table 3

Acid	Product	Behaviour
Hydrochloric acid (1.2 M)	$\text{Ce}_{2.5}\text{Li}_{0.5}\text{S}_4$ and $\text{Ce}_2\text{SrS}_4$	instantaneous reaction and loss of colour
	$\text{Ce}_{0.66}\text{Sm}_{0.33}\text{SF}$	degradation after 1 hour (loss of colour)
Nitric acid (1.1 M)	$\text{Ce}_{2.5}\text{Li}_{0.5}\text{S}_4$ and $\text{Ce}_2\text{SrS}_4$	instantaneous reaction and loss of colour
	$\text{Ce}_{0.66}\text{Sm}_{0.33}\text{SF}$	degradation after 40 min (loss of colour)
Sulphuric acid (1.8 M)	$\text{Ce}_{2.5}\text{Li}_{0.5}\text{S}_4$ and $\text{Ce}_2\text{SrS}_4$	instantaneous reaction and loss of colour
	$\text{Ce}_{0.66}\text{Sm}_{0.33}\text{SF}$	degradation after 30 min (loss of colour)

### Example 15

This example relates to the preparation of a product according to the third  
5 embodiment of the invention.

A sulphide  $\gamma\text{-Sm}_2\text{S}_3$  doped with sodium, of the type of that described in example 2 of  
patent application WO 99/07639 but for which the Na/Sm ratio is 0.2, is used as the starting  
substance.

10

This sulphide is reacted with a samarium fluoride in a quartz tube sealed under  
vacuum at 1,000°C for 24 hours. A product of the formula  $\text{SmSF}$  doped with sodium and  
having the following colorimetric characteristics is obtained:

15  $L = 75$ ;  $a = -2$ ;  $b = 58$ .

### Examples 16 to 20

The procedure is as in example 1 but starting from oxides and fluorides of different  
20 rare earths. The products obtained have an average size of 2  $\mu\text{m}$ .

The colorimetric properties of the products obtained are given in table 4 below.

Table 4

25

Example	Formula	L	a	b	Colour	R400 (%)	R700 (%)
16	LaSF	32.7	-2.6	14.4	pale yellow	5.2	28.4
17	CeSF	39.8	43.4	33.4	red	3.2	50.3
18	PrSF	55.2	-8.2	39.9	yellow	3.5	29.3
19	NdSF	51.1	-8.5	32.5	yellow	2.8	25.3
20	SmSF	79.2	-4.1	73.7	bright yellow	5.1	68.4

### Example 21

This example relates to the preparation of an oxyfluorosulphide of the formula  $\text{Ce}_3\text{S}_2\text{F}_3\text{O}$ .

5 The required stoichiometric amounts of the fluoride  $\text{CeF}_3$ , the sulphide  $\text{Ce}_2\text{S}_3$  and the oxide  $\text{CeO}_2$  are mixed. This mixture is reacted in a quartz tube sealed under vacuum at  $1,200^\circ\text{C}$  for 48 hours. A product having the following colorimetric characteristics is obtained:

$L = 35; a = 40.2; b = 31.3.$

## CLAIMS

- 1- Rare earth fluorosulphide of the formula  $\text{LnSF}$ , in which Ln designates a rare earth, characterized in that it has an average particle size of not more than  $5\text{ }\mu\text{m}$ .
- 5 2- Process for the preparation of a fluorosulphide according to claim 1, characterized in that a rare earth oxyfluoride of the formula  $\text{LnOF}$  is reacted with a mixture of hydrogen sulphide and carbon disulphide.
- 10 3- Process according to claim 2, characterized in that the reaction is carried out at a temperature between  $500^{\circ}\text{C}$  and  $1,200^{\circ}\text{C}$ , preferably between  $900^{\circ}\text{C}$  and  $1,000^{\circ}\text{C}$ .
- 4- Mixed fluorosulphide of rare earths of the formula  $(\text{Ln},\text{Ln}')\text{SF}$ , in which Ln and Ln' designate two rare earths, characterized in that it is in the form of a solid solution.
- 15 5- Fluorosulphide according to claim 4, characterized in that it corresponds to the formula  $(\text{Ln}_{0.66},\text{Ln}'_{0.33})\text{SF}$ .
- 6- Fluorosulphide according to one of claims 4 or 5, characterized in that Ln and Ln' are
- 20 chosen from cerium, samarium, praseodymium and gadolinium.
- 7- Process for the preparation of a fluorosulphide according to claim 5, characterized in that a sulphide of one rare earth  $\text{Ln}_2\text{S}_3$  is reacted with a fluoride of the other rare earth  $\text{Ln}'\text{F}_3$ .
- 25 8- Process according to claim 7, characterized in that the reaction is carried out at a temperature between  $800^{\circ}\text{C}$  and  $1,200^{\circ}\text{C}$ , preferably between  $900^{\circ}\text{C}$  and  $1,000^{\circ}\text{C}$ .
- 9- Process for the preparation of a fluorosulphide according to one of claims 4 to 6, characterized in that a mixed oxyfluoride of rare earths of the formula  $(\text{LnLn}')\text{OF}$  is reacted
- 30 with a mixture of hydrogen sulphide and carbon disulphide.
- 10- Rare earth fluorosulphide, characterized in that it comprises at least one alkali element, and in that it has a structure of the type  $\text{LnSF}$ , tetragonal, space group  $\text{P4/nmm}$ , Ln

designating a rare earth chosen from the group consisting of yttrium and the rare earths Ln between lanthanum and erbium inclusive.

11- Rare earth fluorosulphide, characterized in that it comprises at least one alkali element, and in that it has a hexagonal structure, space group  $P6_322$ , the rare earth belonging to the group of rare earths between holmium and lutecium inclusive and also including yttrium.

12- Process for the preparation of a fluorosulphide according to claim 10 or 11, characterized in that a rare earth sulphide of the formula  $Ln_2S_3$  comprising at least one alkali is reacted with a fluoride of the same rare earth.

13- Rare earth fluorosulphide of the formula  $Ln_2AF_4S_2$ , in which Ln designates at least one rare earth and A designates at least one alkaline earth.

14- Fluorosulphide according to claim 13, characterized in that the alkaline earth is calcium or strontium.

15- Fluorosulphide according to claim 13 or 14, characterized in that the rare earth is cerium or samarium.

16- Process for the preparation of a rare earth fluorosulphide according to one of claims 13 to 15, characterized in that a rare earth sulphide is reacted with a chloride of the same rare earth and a fluoride of the alkaline earth element.

17- Process for the preparation of a rare earth fluorosulphide according to one of claims 13 to 15, characterized in that the rare earth in the form of the metal is reacted with sulphur, a fluoride of the same rare earth and a fluoride of the alkaline earth element.

18- Rare earth oxyfluorosulphide, characterized in that it corresponds to the formula  $Ln_3S_2F_3O$ , in which Ln represents at least one trivalent rare earth.

19- Process for the preparation of an oxyfluorosulphide according to claim 18, characterized in that an oxide of the rare earth, a sulphide of the same rare earth  $Ln_2S_3$  and a fluoride of this rare earth are reacted.

- 20- Use of a fluorosulphide or an oxyfluorosulphide according to one of claims 1, 4 to 6, 10 to 11, 13 to 15 and 18 as a colouring pigment.
- 5 21- Use of a fluorosulphide or an oxyfluorosulphide according to one of claims 1, 4 to 6, 10 to 11, 13 to 15 and 18 as a colouring pigment in plastics materials, paints, finishes, rubbers, ceramics, glazes, papers, inks, cosmetics products, dyestuffs, in the finishing of leathers and in laminated coverings.
- 10 22- Coloured material compositions, in particular of the following type: plastics, paints, finishes, rubbers, ceramics, glazes, papers, inks, cosmetics products, dyestuffs and laminated coverings, characterized in that they comprise a fluorosulphide or an oxyfluorosulphide according to one of claims 1, 4 to 6, 10 to 11, 13 to 15 and 18.

**ABSTRACT OF THE TECHNICAL CONTENT OF THE INVENTION**

**NEW RARE EARTH FLUOROSULPHIDES OR OXYFLUOROSULPHIDES,  
PROCESSES FOR THEIR PREPARATION AND THEIR USE AS A COLOURING  
PIGMENT**

**RHODIA CHIMIE**

The present invention relates to new rare earth fluorosulphides according to four embodiments, new rare earth oxyfluorosulphides, processes for their preparation and their use as a colouring pigment.

The fluorosulphide of the first embodiment corresponds to the formula  $\text{LnSF}$  ( $\text{Ln}$  designates a rare earth) and has an average particle size of not more than  $5\text{ }\mu\text{m}$ . That of the second embodiment is a mixed fluorosulphide of rare earths of the formula  $(\text{Ln},\text{Ln}')\text{SF}$  and is in the form of a solid solution. The fluorosulphide of the third embodiment, according to a first variant, comprises at least one alkali element and has a structure of the type  $\text{LnSF}$ , the rare earth being chosen from yttrium and in the group from lanthanum to erbium inclusive. According to a second variant of this third embodiment the fluorosulphide comprises at least one alkali element and it has a hexagonal structure, space group  $\text{P6}_322$ , the rare earth belonging to the group from holmium to lutecium inclusive and also including yttrium. The fluorosulphide of the fourth embodiment corresponds to the formula  $\text{Ln}_2\text{AF}_4\text{S}_2$ , in which  $\text{A}$  is an alkaline earth. The oxyfluorosulphide corresponds to the formula  $\text{Ln}_3\text{S}_2\text{F}_3\text{O}$ , in which  $\text{Ln}$  represents at least one trivalent rare earth.

R99058

022701-967

022701-967  
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My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**RARE EARTH FLUOROSULPHIDES OR OXYFLUOROSULPHIDES, METHODS FOR  
PREPARING SAME AND USE THEREOF AS DYEING PIGMENT**

the specification of which (check only one item below):

- ☐ is attached hereto.
- ☐ was filed as United States application  
Number \_\_\_\_\_ on \_\_\_\_\_  
and was amended \_\_\_\_\_ on \_\_\_\_\_ (if applicable).
- ☒ was filed as PCT international application  
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I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §§119 (a)-(d), 172 or 365 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

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			Yes	No

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Attorney's Docket No. 022701-967  
Page 2 of 3

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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